

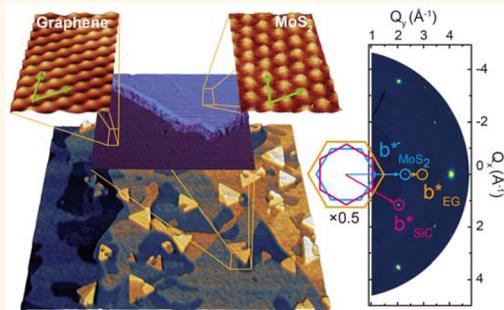
Rotationally Commensurate Growth of MoS₂ on Epitaxial Graphene

Xiaolong Liu,^{†,¶} Itamar Balla,^{‡,¶} Hadallia Bergeron,[‡] Gavin P. Campbell,[‡] Michael J. Bedzyk,^{*,†,‡,§} and Mark C. Hersam^{*,†,‡,||,⊥}

[†]Graduate Program in Applied Physics, [‡]Department of Materials Science and Engineering, [§]Department of Physics, ^{||}Department of Chemistry, and [⊥]Department of Medicine, Northwestern University, Evanston, Illinois 60208, United States

Supporting Information

ABSTRACT: Atomically thin MoS₂/graphene heterostructures are promising candidates for nanoelectronic and optoelectronic technologies. Among different graphene substrates, epitaxial graphene (EG) on SiC provides several potential advantages for such heterostructures, including high electronic quality, tunable substrate coupling, wafer-scale processability, and crystalline ordering that can template commensurate growth. Exploiting these attributes, we demonstrate here the thickness-controlled van der Waals epitaxial growth of MoS₂ on EG *via* chemical vapor deposition, giving rise to transfer-free synthesis of a two-dimensional heterostructure with registry between its constituent materials. The rotational commensurability observed between the MoS₂ and EG is driven by the energetically favorable alignment of their respective lattices and results in nearly strain-free MoS₂, as evidenced by synchrotron X-ray scattering and atomic-resolution scanning tunneling microscopy (STM). The electronic nature of the MoS₂/EG heterostructure is elucidated with STM and scanning tunneling spectroscopy, which reveals bias-dependent apparent thickness, band bending, and a reduced band gap of ~0.4 eV at the monolayer MoS₂ edges.



KEYWORDS: transition metal dichalcogenide, silicon carbide, scanning tunneling microscopy, synchrotron X-ray scattering, chemical vapor deposition, van der Waals heterostructure

Vertical heterostructures composed of stacked two-dimensional (2D) materials allow the exploration of fundamental interfacial interactions and novel electronic functionality. From among the 2D material library consisting of semimetals (*e.g.*, graphene^{1,2}), insulators (*e.g.*, boron nitride³ and Bi₂Se₃⁴), and semiconductors (*e.g.*, black phosphorus^{5–7} and transition metal dichalcogenides^{8,9}), the MoS₂/graphene heterostructure^{10,11} shows great potential for next generation electronic and optoelectronic applications due to complementary carrier mobilities and optical responsivities.¹² Additionally, the MoS₂/graphene heterostructure has been shown to be an excellent catalyst for hydrogen evolution reactions¹³ and a promising anode material for Li-ion batteries.¹⁴

The properties of MoS₂/graphene heterostructures depend strongly on the underlying substrate and the graphene synthesis technique. Epitaxial graphene (EG) grown on SiC by the preferential thermal desorption^{15,16} of silicon from SiC not only offers uniform large-area synthesis of graphene but also provides technological advantages over alternative methods such as chemical vapor deposition (CVD) and mechanical exfoliation. For example, fine control of the growth temperature enables homogeneous monolayer or bilayer EG at the wafer scale,^{17–19} while postannealing in hydrogen allows decoupling

of EG from the underlying SiC substrate.² The high quality and cleanliness of EG is evidenced by its high carrier mobility²⁰ of 45 000 cm² V^{−1} s^{−1} and observation of the quantum Hall effect.²¹ Furthermore, the interaction between graphene and the SiC substrate can be tailored *via* intercalation of different atomic species.²²

Given the underlying SiC substrate as well as the different electronic characteristics of EG (*e.g.*, substrate-induced n-type doping^{23,24}), CVD synthesis of MoS₂ on EG is expected to differ from that on graphite or CVD graphene, giving rise to novel structural and electronic interactions between the two materials. While MoSe₂ has been grown on EG by molecular beam epitaxy,^{25,26} recent reports of MoS₂ grown by CVD on graphite^{9,27,28} and EG^{29,30} resulted in non-epitaxial growth, where the orientation of the MoS₂ crystals was not controlled. Furthermore, the atomic-scale electronic and structural properties of MoS₂/EG heterostructures have not been thoroughly established. Toward these ends, we report here the rotationally commensurate growth of atomically thin MoS₂ crystals on EG

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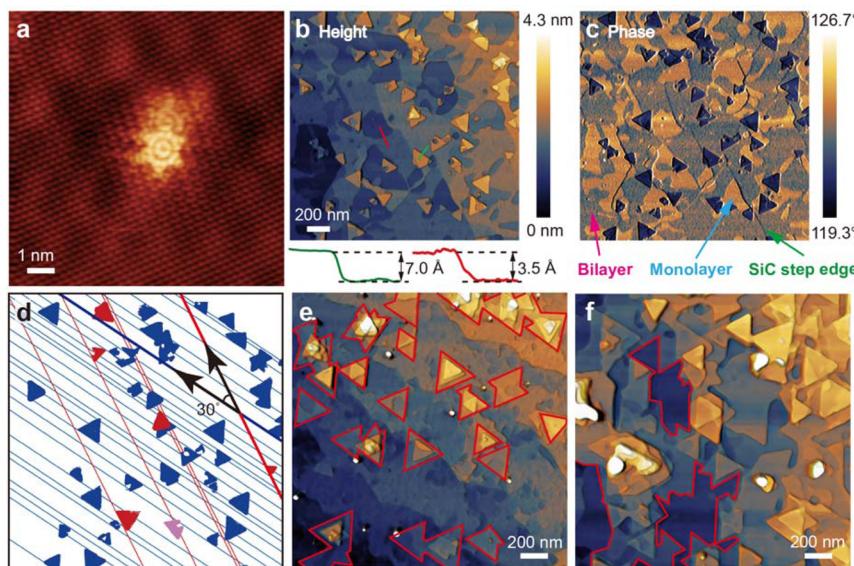


Figure 1. CVD-grown MoS₂ on EG at different conditions. (a) UHV STM image of EG before growth of MoS₂, showing a typical rotational grain boundary on EG ($V_{\text{sample}} = -0.1$ V, $I_{\text{tunneling}} = 0.4$ nA). EG lattice and underlying SiC ($6\sqrt{3} \times 6\sqrt{3}$)R30° reconstruction are clearly observed. (b) AFM height and (c) phase images of MoS₂/EG grown at 43 Torr. Line profiles show monolayer MoS₂ (green) and graphene (red) thicknesses. The contrast between bilayer and monolayer regions of EG is more obvious in the phase image. (d) Extraction of edge orientations of MoS₂ crystals in (b), showing two predominant registrations of MoS₂ on EG. (e) AFM images of MoS₂/EG grown at 50 Torr and (f) 100 Torr, showing multilayer growth and larger crystal domain size. The interface between EG and MoS₂ is highlighted in red.

by van der Waals epitaxy. We investigate the electronic and structural properties of the resulting MoS₂/EG heterostructures by a comprehensive suite of methods including atomic force microscopy (AFM), ultrahigh vacuum (UHV) scanning tunneling microscopy and spectroscopy (STM/STS), synchrotron X-ray scattering, *in situ* X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. In addition to the inherent advantages of van der Waals epitaxy (e.g., reduced defect density,³¹ sharper interfaces,³² and consistent material quality), the registry between the MoS₂ and EG allows for the study of crystal orientation-dependent properties (e.g., anisotropic thermal conductance of MoS₂³³) and specific types of grain boundaries (e.g., mirror twin grain boundaries³⁴) for fundamental studies³⁴ and electronic applications.³⁵ Specifically, the epitaxial growth of MoS₂ hinders the formation of tilt grain boundaries that degrade in-plane electrical conductivity and favors the formation of mirror twin grain boundaries that preserve in-plane electrical conductivity.³⁴ It has also been demonstrated that the type of grain boundary affects the optical properties of MoS₂.³⁴ Therefore, the ability to synthesize rotationally commensurate MoS₂ domains on EG facilitates ongoing efforts to realize reproducibly high-performance MoS₂/graphene electronic and optoelectronic devices.

RESULTS AND DISCUSSION

CVD growth of MoS₂ on EG is performed at a variety of conditions in order to tune and optimize the MoS₂ film thickness. Figure 1a is an STM image of EG prior to MoS₂ growth that contains a rotational grain boundary on EG with atomic structure consistent with that in previous literature.^{36,37} In addition to the rotational grain boundary defect, the graphene lattice and underlying ($6\sqrt{3} \times 6\sqrt{3}$)R30° SiC reconstruction are clearly resolved. Figure 1b,c shows the AFM topography and phase images, respectively, of MoS₂ grown on EG at 43 Torr (detailed growth conditions are given in Methods; additional AFM images are provided in Figure S1).

The measured thickness of a MoS₂ triangular domain is 7.0 Å, as indicated by the green line profile in Figure 1b, corresponding to monolayer MoS₂.³⁸ Monolayer and bilayer graphene regions are observed in the topography image (Figure 1b) and are more clearly distinguished in the phase image (Figure 1c), where monolayer regions are brighter. The measured step height is 3.5 Å, as indicated by the red line profile in Figure 1b, which is also in agreement with the literature.³⁹ Figure 1d extracts the edge orientations of the MoS₂ triangles shown in Figure 1b by plotting a line along one edge of each triangle. A large majority of the triangles have parallel edges as indicated by the blue lines, while a few triangles, indicated in red, have edges rotated by 30°. The rare occurrence of a third rotational orientation of a MoS₂ triangular domain is shown in pink. From this analysis, it is apparent that there are two predominant types of azimuthal registration of MoS₂ on EG. This crystal orientation alignment is attributed to van der Waals epitaxy,³² which accommodates the large lattice mismatch (~28%) between graphene and MoS₂, as will be further discussed below.

Examination of the growth nucleation sites reveals that MoS₂ growth preferentially (but not exclusively) initiates at the step edges of the underlying SiC and graphene. This observation can be explained by the higher reactivity of graphene as a function of local curvature^{40,41} at SiC steps and exposed graphene edges.⁴² Indeed, STS spatial maps reveal different electronic properties of the graphene wrinkles and edges compared to the flat regions, as shown in Figure S2. Higher growth pressures of 50 and 100 Torr result in bilayer and pyramid-like multilayer growth with larger domain sizes and higher coverage, as shown in Figure 1e,f, respectively, where the interface between EG and MoS₂ is highlighted in red. Higher synthesis pressure increases the local concentration of growth precursors and facilitates growth on the MoS₂ basal planes, resulting in multilayer crystals.^{43,44} Hence, by tuning the growth pressure, the thickness of the MoS₂ domains can be controlled.

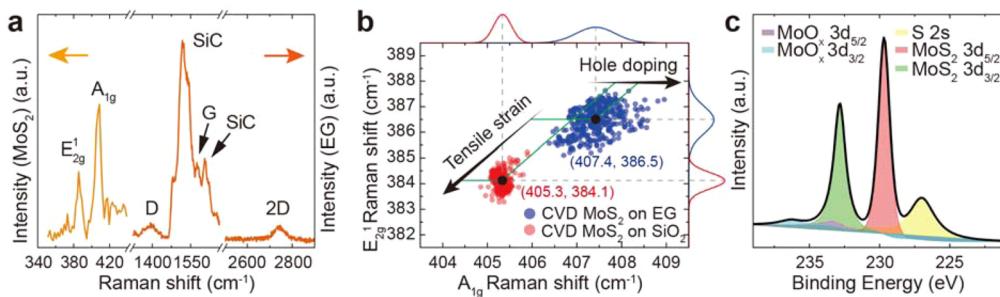


Figure 2. Raman and XPS characterization of a MoS₂/EG heterostructure with primarily monolayer MoS₂. (a) Raman spectrum of MoS₂/EG showing the E_{2g}¹ and A_{1g} peaks of MoS₂, and the D, G, and 2D peaks of EG. (b) Strain and doping analysis of CVD MoS₂ on EG in comparison to CVD MoS₂ on SiO₂ from spatial Raman mapping measurements. (c) *In situ* XPS spectrum of MoS₂/EG after annealing at 205 °C for 6 h in UHV, showing characteristic Mo 3d doublets and minimal MoO_x peaks.

The as-grown MoS₂/EG heterostructure is characterized by Raman spectroscopy as shown in Figure 2a. Raman signatures of MoS₂ (A_{1g} at 407.2 cm⁻¹, E_{2g}¹ at 386.4 cm⁻¹) and graphene (D at 1391.2 cm⁻¹, G at 1575.4 cm⁻¹, 2D at 2740.8 cm⁻¹) are clearly resolved. Several factors affect the positions of the A_{1g} and E_{2g}¹ modes, including layer number,⁴⁵ strain,⁴⁶ and doping.⁴⁷ Using a method previously demonstrated on graphene,⁴⁸ the strain and doping effects of MoS₂ on EG can be deconvolved. For this analysis, a sample of CVD-grown MoS₂ on SiO₂ was prepared (see the optical microscopy and AFM images in Figure S3). To circumvent the MoS₂ thickness effects on the Raman peak positions, the two samples were prepared under growth conditions that yield primarily MoS₂ monolayers. Spatial Raman mapping of the MoS₂/EG and MoS₂/SiO₂ samples was then performed, and the E_{2g}¹ versus A_{1g} mode positions are plotted in Figure 2b. It has been shown previously that A_{1g} and E_{2g}¹ modes shift up with compressive strain⁴⁶ and down with tensile strain.^{49,50} Since the reported ratio of the shifting rates of E_{2g}¹ to A_{1g} under biaxial strain is ~1.5⁴⁶ and hole doping shifts up the A_{1g} mode while the E_{2g}¹ mode remains unchanged,⁴⁷ pure strain and doping effects are represented by two arrowed lines with slopes of 1.5 and 0 in Figure 2b, respectively. Thus, in comparison to MoS₂ on SiO₂, MoS₂ grown on EG has higher hole doping and lower tensile strain. The higher hole doping level may be due to differences in charge transfer for the two systems.^{51,52} In addition, the lower tensile strain can be explained by the fact that while MoS₂/SiO₂ is under tensile strain,⁵³ MoS₂/EG is strain-free as will be demonstrated later by X-ray scattering. Given that the difference in the E_{2g}¹ mode positions between the two systems is 2.4 cm⁻¹, the corresponding tensile strain of MoS₂/SiO₂ is ~0.2%.⁴⁶

The electronic properties of the MoS₂/EG heterostructure are further explored using a custom-designed UHV STM with a base pressure of ~6 × 10⁻¹¹ Torr at room temperature.⁵⁴ Prior to scanning, the sample is degassed at 205 °C for 6 h in UHV and then characterized by *in situ* XPS. The molybdenum core level XPS spectrum is shown in Figure 2c, with detailed subpeak positions provided in the Methods section. The doublets of the Mo 3d orbital corresponding to MoS₂ are considerably higher than those of MoO_x, indicating the high quality of the MoS₂ crystals. Figure 3a is an STM image showing a typical monolayer MoS₂ crystal on EG. The (6 $\sqrt{3}$ × 6 $\sqrt{3}$)R30° reconstruction of EG is seen in the bottom half of the image. Nine STS spectra taken at different positions on the MoS₂ crystal far from its edges are shown in Figure 3b. The band gap is uniformly ~2 eV across a single domain, which falls

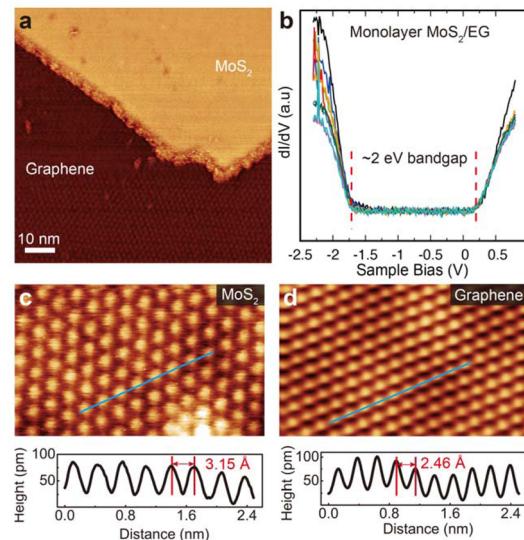


Figure 3. UHV STM/STS characterization of MoS₂/EG. (a) STM image of the corner of a monolayer MoS₂ crystal domain on EG, where the underlying SiC (6 $\sqrt{3}$ × 6 $\sqrt{3}$)R30° reconstruction is seen at the bottom ($V_{\text{sample}} = 0.2$ V, $I_{\text{tunneling}} = 50$ pA). (b) STS dI/dV spectra taken at nine different positions on the MoS₂ crystal domain far away from the edges, showing a uniform band gap of ~2 eV. (c,d) Atomic-scale images and line profiles of (c) MoS₂ ($V_{\text{sample}} = -0.2$ V, $I_{\text{tunneling}} = 50$ pA) and (d) EG ($V_{\text{sample}} = -0.1$ V, $I_{\text{tunneling}} = 0.4$ nA), demonstrating aligned lattice orientations.

within the range of reported STS band gaps of monolayer MoS₂ on graphite (1.9 eV,²⁸ 2.15 eV,⁹ and 2.4 eV²⁷). Thermal broadening and energy uncertainty resulting from the small tunneling junction may explain the small deviations in the STS-measured band gap.⁵⁵ Atomic resolution images of a MoS₂ triangular domain and EG in Figure 3a are shown in Figure 3c,d, respectively. From the line profiles, the periods of atomic corrugation for MoS₂ and EG are measured to be 3.15 and 2.46 Å, corresponding to their respective lattice constants. Both the MoS₂ and EG atomic-scale STM images show six-fold symmetry and rotational commensurability as a result of van der Waals epitaxy. Figure 4a contains STS mappings of the corner of a MoS₂ triangle overlaid on three-dimensionally rendered STM height images taken at $V_{\text{sample}} = -0.3$ V and $V_{\text{sample}} = 0.3$ V. Since the differential tunneling conductance measured by STS is proportional to the sample density of states (DOS), the semiconducting nature of MoS₂ and semimetallic

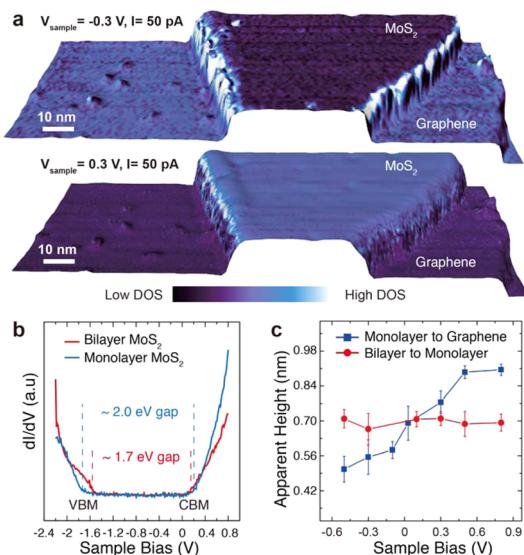


Figure 4. Electronic structure of MoS₂/EG. (a) STS mappings overlaid on three-dimensionally rendered topography images of MoS₂/EG at sample biases of -0.3 V and $+0.3$ V, showing different relative DOS between MoS₂ and EG. (b) STS spectra taken on monolayer and bilayer MoS₂, showing a smaller band gap of ~ 1.7 eV for bilayer MoS₂. (c) Bias-dependent apparent thickness of monolayer MoS₂ on EG and apparent height of a monolayer to bilayer MoS₂ step edge.

nature of EG give rise to the inversion of the relative DOS at these two biases.

STS spectra for monolayer and bilayer MoS₂ are shown in Figure 4b. Compared to monolayer, bilayer MoS₂ has a reduced band gap of ~ 1.7 eV, resulting from an increased valence band maximum (VBM) and a subtle decrease of the conduction band minimum (CBM). Although the physical thickness of monolayer MoS₂ is ~ 7 Å, the apparent height measured by STM depends on applied bias, as indicated by the blue curve in Figure 4c. This convolution of topography and electronic structure in constant current STM imaging is well-known and often pronounced for ultrathin films.⁵⁶ Qualitatively, at high positive bias, the MoS₂ conduction band shows higher DOS

than EG, as shown in Figure 4a, which implies that the tip retracts more on MoS₂ than EG to maintain a constant current. On the other hand, at low negative bias, the opposite occurs as EG shows higher DOS than MoS₂ (Figure 4a). This change in relative DOS and the proximity of the MoS₂ CBM to zero makes the MoS₂ apparent thickness larger at high positive bias and smaller at negative bias than its physical thickness. Also shown in Figure 4c is the measured apparent height of the step edge from bilayer to monolayer MoS₂ at different sample biases. Since bilayer and monolayer MoS₂ have similar DOS in the measured range, the apparent thickness does not vary significantly from its physical thickness.

The effects of edges^{57,58} on the electronic properties of MoS₂ are also investigated by spatially resolved STS spectra. A series of vertically offset STS spectra taken across an EG to MoS₂ step edge are shown in Figure 5a, with their respective positions marked by colored dots in the inset. The distance from each measured point to the step edge is further indicated in the figure. These spectra reveal that the band gap increases gradually to ~ 2 eV after moving ~ 5 nm into the MoS₂ flake. The dashed black lines denote the VBM and CBM of each spectrum. Both band edges shift to higher energy when approaching the MoS₂ edge from the interior, similar to the band bending observed for MoS₂ on graphite.⁹ However, the gradual decrease of the band gap (*i.e.*, faster increase of the VBM than the CBM) when approaching the MoS₂ edge differs from the nearly constant band gap observed in the band bending region of MoS₂ on graphite.⁹ Similar STS spectra taken across the transition from bilayer to monolayer MoS₂ are shown in Figure 5b. In this case, the band gap changes from ~ 1.7 eV on bilayer MoS₂ to ~ 2.0 eV on monolayer MoS₂. However, at the edge position, the band gap drops significantly to ~ 0.4 eV. This large decrease in the band gap is consistent with edge states⁵⁸ that have been predicted by density functional theory (DFT) to reduce the band gap of MoS₂ to 0.43 eV at the monolayer to bilayer step edge⁵⁹ and below 0.6 eV at isolated MoS₂ monolayer edges.⁵⁷

To verify that these local AFM and STM observations persist over the entire sample, synchrotron grazing-incidence wide-angle X-ray scattering (GIWAXS) is employed to investigate the van der Waals epitaxy of MoS₂ on EG. A schematic of

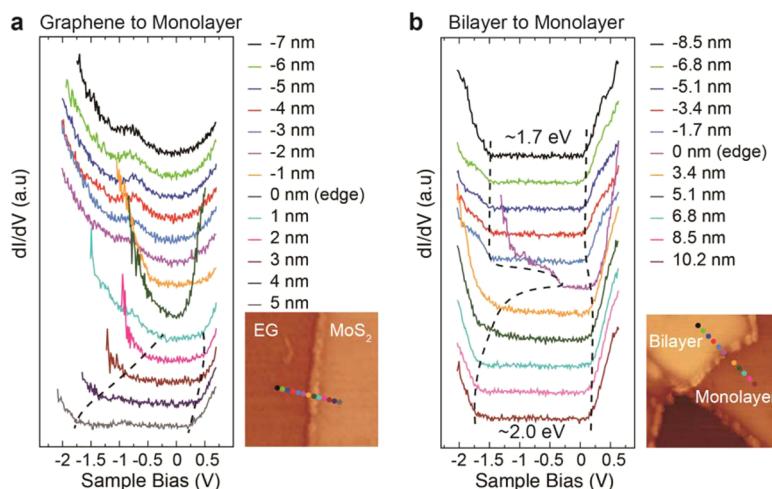


Figure 5. STS line scans across MoS₂ edges. (a) STS spectra taken across a monolayer MoS₂ edge from EG. (b) STS spectra taken across a step edge from bilayer to monolayer MoS₂, showing band bending and decreased band gap near the edge to ~ 0.4 eV.

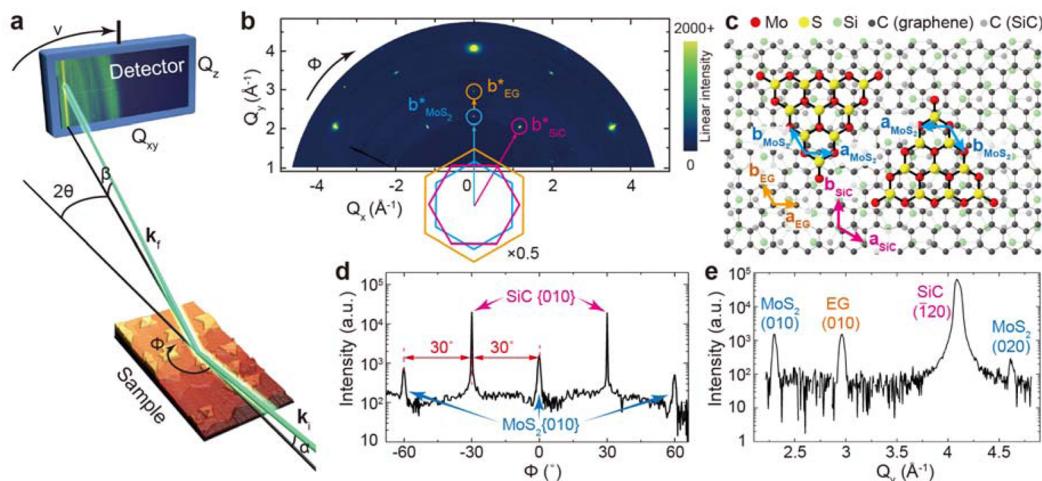


Figure 6. Rotationally commensurate van der Waals epitaxy of MoS₂ on EG. (a) Schematic of GIWAXS measurement: k_i , incident wave vector; k_f , scattering wave vector; α , incident angle; β , out-of-plane angle; 2θ , in-plane angle; φ , sample rotation angle; ν , detector rotation angle. (b) Q_{xy} 2D reciprocal space map of MoS₂/EG projected from $Q_z = 0.08$ to 0.12 \AA^{-1} by synchrotron GIWAXS. The b^* reciprocal space vectors are indicated by arrows. (c) Real-space model of the MoS₂/EG heterostructure with MoS₂ lattice aligned with that of EG. (d) Projected first-order peaks of MoS₂ and SiC onto ϕ , showing sharp distributions. (e) Referring to (b), in-plane scattered intensity along the Q_y direction at $Q_x = 0$. The determined real-space lattice constants of MoS₂, EG, and SiC are 3.16 ± 0.01 , 2.46 ± 0.01 , and $3.07 \pm 0.01 \text{ \AA}$, respectively.

GIWAXS is shown in Figure 6a, and experimental details are outlined in the Methods section. In GIWAXS, the incident X-ray beam is at an incident angle of $\alpha = 0.14^\circ$, slightly below the critical angle of total external reflection of the substrate. The out-of-plane angle β and in-plane angle 2θ define the position at which the scattered X-ray wave vector k_f intersects the plane of the 2D detector. The Q_{xy} 2D reciprocal space map of the MoS₂/EG/SiC structure projected from $Q_z = 0.08$ to 0.12 \AA^{-1} is shown in Figure 6b, with first-order spots of MoS₂, EG, and SiC identified. The blue, orange, and magenta arrows indicate the reciprocal lattice vectors b^* for MoS₂, EG, and SiC, respectively. As seen by the reciprocal space points, the reciprocal lattices for MoS₂ and EG are aligned, whereas SiC has a well-known 30° rotation with respect to EG.⁶⁰ This observation indicates that the majority of the MoS₂ crystals are epitaxially grown along the EG lattice direction with matching six-fold symmetry, confirming the symmetry inferred from AFM (Figure 1 and Figure S1) and STM (Figure 3). The real-space structure reconstructed for such aligned MoS₂ growth is shown in Figure 6c, where the two MoS₂ triangles represent the preferred orientations in the epitaxial MoS₂/EG heterostructure shown in Figure 3c,d. Projected first-order MoS₂ and SiC peaks onto ϕ are included in Figure 6d to examine the angular distribution. The relative angle between the MoS₂ and SiC lattices is indeed $30 \pm 0.3^\circ$, which is a much narrower azimuthal distribution than that of CVD MoS₂ grown on sapphire.⁶¹ The full width at half-maxima of the first-order MoS₂, EG, and SiC peaks as a function of ϕ are 0.7 , 0.5 , and 0.05° (limited by X-ray optics), respectively, which confirms that the MoS₂ is in excellent registry with EG.

Figure 6e shows the scattered intensity from the 2D reciprocal space map of Figure 6b collected along Q_y at $Q_x = 0$. The real-space lattice constants calculated for MoS₂, EG, and SiC are 3.16 ± 0.01 , 2.46 ± 0.01 , and $3.07 \pm 0.01 \text{ \AA}$, respectively. To gain more insight into the structure of MoS₂ on EG, in-plane X-ray diffraction of MoS₂/EG and bulk MoS₂ was performed (Figure S4). The resulting lattice constants of MoS₂/EG and bulk MoS₂ are 3.160 ± 0.005 and 3.159 ± 0.006

\AA , which indicate a relaxed in-plane structure of MoS₂ on EG similar to its bulk counterpart. The lack of in-plane strain in the synthesized MoS₂ 2D crystals can be explained by total strain relaxation in the van der Waals gap, analogous to a buffer layer alleviating the strain in conventional epitaxy.⁶²

As indicated by the red MoS₂ triangles in Figure 1d, there is a secondary, less preferred registration between MoS₂ and EG, where the MoS₂ lattice is rotated by 30° . To examine the relative amount of 30° rotated growth, GIWAXS data of the MoS₂(010) peak taken along the EG[010] direction (aligned growth, blue) and the SiC[010] direction (30° rotated growth, red) are shown in Figure 7. From the integrated intensities of the two MoS₂ peaks, the amount of MoS₂ with lattice 30° rotated from the EG lattice is determined to be $14 \pm 4\%$ of the total intensities, while the aligned growth is found to be dominant at $86 \pm 4\%$. This large-area GIWAXS result is consistent with the orientation distribution of MoS₂ domains

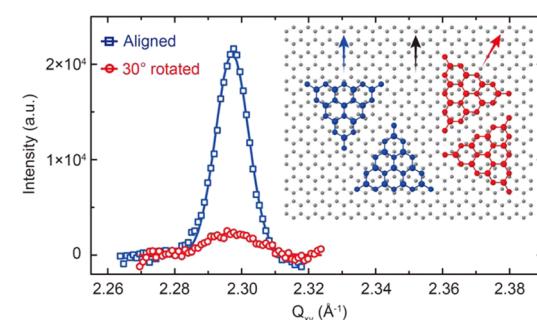


Figure 7. Examination of the growth orientation of MoS₂. GIWAXS data of the MoS₂(010) peak taken along the EG[010] direction (aligned growth, blue) and the SiC[010] direction (30° rotated growth, red). The integrated intensities of these two peaks are 2.6×10^5 and 4.2×10^4 , respectively. Inset: Schematic of the two growth orientations of MoS₂ on EG. The armchair directions of MoS₂ from aligned (blue) and 30° rotated (red) growth are indicated by the blue and red arrows, respectively. The black arrow indicates the armchair direction of EG.

shown in the AFM images in Figures 1 and S1. Thus, in Figure 1d, we attribute the majority blue MoS₂ triangles to aligned growth, and the minority red triangles to 30° rotated growth. The inset of Figure 7 shows the schematic of these two registrations, where the blue, black, and red arrows indicate the armchair directions of aligned MoS₂, EG, and 30° rotated MoS₂, respectively. These two growth orientations have also been observed previously for MoS₂ grown on sapphire.^{61,63} Rare deviations in the preferred orientations, such as the pink MoS₂ crystal domain shown in Figure 1d, indicate lack of registry of the MoS₂ domain with the EG and can be attributed to local disturbances in the substrate surface. These occurrences were not frequent enough to produce detectable scattered X-ray intensity.

CONCLUSIONS

In summary, a 2D heterostructure of rotationally commensurate MoS₂ on EG has been grown *via* van der Waals epitaxy with controlled thickness. The structural and electronic quality of these samples has been probed down to the atomic scale using a combination of UHV STM/STS and synchrotron X-ray scattering. MoS₂ is found to preferentially grow with lattice aligned with EG. The relative amount of a less preferred 30° rotated growth is also determined. Furthermore, Raman spectroscopy and in-plane X-ray diffraction show that the MoS₂ is nearly strain-free, thus providing an ideal system for probing the fundamental properties of two-dimensional MoS₂. For example, spatially resolved STS measurements across MoS₂ step edges reveal band gap narrowing that is in close agreement with DFT calculations. Overall, this study suggests that EG may be a promising substrate for van der Waals epitaxial growth of other emerging two-dimensional nanomaterials in addition to providing a well-defined platform for the future study and application of MoS₂/graphene heterostructures.

METHODS

Synthesis of Epitaxial Graphene. Following a similar procedure of producing EG on 6H-SiC (0001) as outlined previously,^{15,16} an n-type 4H-SiC (0001) wafer (Cree Inc.) degreased in an acetone and isopropyl alcohol (IPA) sonication bath was degassed at 550 °C for 12 h under UHV conditions ($\sim 5 \times 10^{-10}$ Torr). Few-layer EG was grown on the Si face by thermal desorption of Si atoms at 1270 °C for 20 min. The first carbon-rich buffer layer has a $6\sqrt{3} \times 6\sqrt{3}$ unit cell, which is known as the $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ reconstruction.

Synthesis of MoS₂. Molybdenum trioxide (MoO₃, 99.98% trace metal Sigma-Aldrich) was placed in the middle of the hot zone of a Lindberg/Blue 1 in. quartz tube furnace in an alumina boat 2.5 cm upstream of a 5 mm × 9 mm EG substrate (graphitized Si face is facing up). The sulfur powder (Sigma-Aldrich) in an alumina boat was placed 30 cm upstream of the MoO₃ boat under a proportional integral derivative temperature-controlled heating belt. The tube was initially pumped to a base pressure of ~ 50 mTorr and purged with Ar gas to 400 Torr. During the anneal prior to the reaction and during the reaction itself, the pressure was kept constant at 43 Torr (to yield mostly monolayer MoS₂ crystals) using a needle valve controller and Ar carrier gas flowing at 25 sccm. The MoO₃ and EG substrate were annealed for 20 min at 150 °C (with a 5 min ramp to 150 °C from room temperature) to eliminate residual water and physisorbed contaminants in the tube and on the substrate. Subsequently, the furnace was heated to a maximum temperature of 800 °C at a rate of 12 °C/min. Once the target temperature was reached, the furnace was kept at 800 °C for 20 min and cooled down naturally to room temperature. Concurrently, the sulfur was annealed under the same inert conditions for 49 min at 50 °C (with 5 min ramp to 50 °C from room temperature) and brought to a maximum temperature of 140 °C

at a rate of 4 °C/min. The sulfur ramp to 140 °C began when the furnace was approximately at 500 °C. The sulfur was then kept at the maximum temperature for 23 min.

For the synthesis of MoS₂ on SiO₂, a 4 cm × 1 cm 300 nm thick SiO₂/Si wafer (SQI Inc.) was sonicated in acetone and IPA bath for 10 min, rinsed with deionized water, and treated with oxygen plasma for 1 min. The wafer was then placed in close proximity to the MoO₃ boat, and the same growth procedure was applied with a change to the following parameters: a reaction chamber pressure of 150 Torr was maintained instead of 43 Torr, and the sulfur was brought to a maximum temperature of 150 °C instead of 140 °C at a rate of 4.5 °C/min.

Scanning Tunneling Microscopy and Spectroscopy. A home-built UHV STM system⁵⁴ integrated with a preparation chamber, an XPS chamber, and a load lock was utilized for STM, STS, and XPS measurements. The microscope adopts a Lyding design⁶⁴ with a bias voltage applied to the sample with respect to the grounded tip. The base pressure in the STM chamber was $\sim 6 \times 10^{-11}$ Torr. Both electrochemically etched W and PtIr tips (Keysight) were used. STS spectra and mappings were taken with a lock-in amplifier (SRS model SR850) with a modulation frequency of ~ 8.5 kHz and rms amplitude of 30 mV. The experimental variability of band gap measurements in this work is estimated to be 0.08 eV. This estimate is based on the standard deviation of band gap measurements (Figure S5) from 80 STS spectra on multiple monolayer MoS₂ domains. Specifically, these measurements imply that the band gap is 2.01 ± 0.08 eV. Nanonis SPM control electronics were used for data collection. The STM system was calibrated using atomic resolution EG for the *x*-*y* piezo and Ag(111) single-crystal monolayer step height for the *z* piezo.

Atomic Force Microscopy. AFM experiments were carried out on an Asylum Cypher AFM in tapping and contact modes. Si cantilevers NCHR-W from NanoWorld with a resonant frequency of ~ 320 kHz were used for tapping mode imaging, and PPP-CNTSCAu cantilevers from NanoSensors were used for contact mode imaging (2–5 nN force was applied). The images were taken with a pixel resolution of 512 × 512 or 1024 × 1024 at a scanning rate of ~ 1 Hz.

X-ray Photoelectron Spectroscopy. XPS spectra were taken at a base pressure of $\sim 4 \times 10^{-10}$ Torr with an Omicron DAR 400 M X-ray source, XM 500 X-ray monochromator, and EA 125 energy analyzer. The XPS system was integrated with the UHV STM system for *in situ* measurements. The binding energy resolution was 0.1 eV. Ten scans were averaged for each core level spectrum. All subpeaks were fit with a modified Shirley background in Avantage (Thermo Scientific) software after calibrating the spectra to graphene carbon at 284.5 eV. The peaks positions are as follow: S 2s, 227.0 eV; MoS₂ 3d_{5/2}, 229.7 eV; MoS₂ 3d_{3/2}, 232.8 eV; MoO_x 3d_{5/2}, 233.1 eV; and MoO_x 3d_{3/2}, 236.3 eV.

Raman Spectroscopy. Raman measurements were carried out on a Horiba Scientific XploRA PLUS Raman microscope with excitation laser line of 532 nm (with spot size $\sim 1 \mu\text{m}^2$) in ambient conditions. The Raman signal was collected using a 100× Olympus objective (NA = 0.9) and dispersed by 1800 grooves/mm grating to a Syncerity CCD detector with a corresponding spectral resolution finer than 2 cm⁻¹. A laser power of about 1 mW was used with an acquisition time of ~ 15 s to avoid heating effects. The Raman spectra were collected in the spatial mapping mode with step sizes of ~ 500 nm. The MoS₂ Raman modes of E_{2g}¹ and A_{1g} on both the EG/4H-SiC and SiO₂/Si substrates were fitted with Lorentzian functions and calibrated against the 4H-SiC band⁶⁵ at 776.65 cm⁻¹ and Si band at 520.7 cm⁻¹, respectively.

Synchrotron X-ray Scattering. The GIWAXS data of MoS₂/EG/SiC were collected at sector 12-ID-C at the Argonne National Laboratory Advanced Photon Source. The 23.5 keV monochromatic X-ray beam was defined using slits of 50 μm × 2 mm to have a 5 mm × 2 mm footprint on the sample at incident angle $\alpha = 0.14^\circ$. The incident flux was 4×10^{12} photons/s. As depicted in Figure 6a, a 100 K Pilatus area detector was mounted on a rotating ν -arm positioned at approximately 354 mm from the sample to collect the GIWAXS signal. Data within $q = 2.2$ to 4.8 \AA^{-1} in Figure 6 was collected at $\nu = 10.262^\circ$ relative to the direct beam. The sample was kept under a helium

environment and placed on a ϕ rotation stage. The 33-ID-C line was used to collect high-resolution grazing-incidence X-ray scattering and diffraction data from the bulk MoS₂ single crystal and MoS₂/EG samples. Monochromatic 10 keV X-rays were focused to $70 \mu\text{m} \times 30 \mu\text{m}$ using a horizontal Kirkpatrick-Baez mirror with a flux of 2×10^{11} photons/s. Data were collected using a Dectris 100 K Pilatus area detector mounted on a Newport 6-circle goniometer. The reciprocal space map in Figure 6b was generated using the Ewald sphere construction method, wherein pixels from $Q_z = 0.08$ to 0.12 \AA^{-1} were projected onto a 2D reciprocal space map using interpolation plots in Mathematica. Peaks were fit using the Gaussian fitting function in MATLAB.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acsnano.5b06398](https://doi.org/10.1021/acsnano.5b06398).

Additional information including supplemental AFM, STM/STS, optical images, and lattice constants analysis ([PDF](#))

AUTHOR INFORMATION

Corresponding Authors

*E-mail: bedzyk@northwestern.edu.

*E-mail: m-hersam@northwestern.edu.

Author Contributions

†X.L. and I.B. contributed equally.

Notes

The authors declare no competing financial interest.

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